

# FINAL PROGRESS REPORT

In-Site Polarization Modulated FTIR  
and  
Differential Electrochemical Mass Spectroscopy

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# REPORT DOCUMENTATION PAGE

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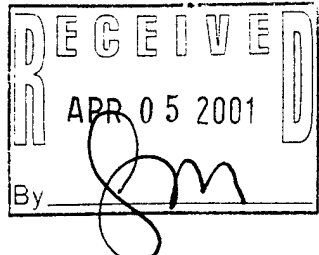
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13. ABSTRACT (Maximum 200 words)

We recently report the electrochemical promotion of the heterogeneously catalyzed isomerization of 1-butene to *cis* -and *trans* butene with *p* values of 38 and 46, respectively, at the remarkably low temperature of 70°C using Nafion as the electrolyte in a fuel cell configuration. This was the first reported case of a NEMCA promoted unimolecular and non-redox reaction concomitant with the reduction of butene to butane. We now present isotopic mass spectral and FTIR data confirming the mechanism involves abstraction of a proton from the catalytic surface for Markovnikov addition to the C-1 carbon concomitant with removal of a proton from C-3 to yield the isomer. This striking example of an acid catalyzed reaction at a metal surface is facilitated by the use of the super acidic Nafion electrolyte.

Material: 1-butene: *cis* -2-butene; *trans*-2-butene; Nafion; Pd; Deuterium; D2O



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## In-Site Polarization Modulated FTIR and Differential Electrochemical Mass Spectroscopy

Award Number: DAAG55-97-1-0198

### (4) Statement of the problems studied

This program was a DURIP grant for equipment to be used for the development of in-situ methods of analysis of products formed at fuel cell electrode surfaces. In-situ methods are required in the case of fuel cell catalysis because of the peculiarities of the electrode systems used in fuel cells. In polymer electrode fuel cells there are no mobile anions. Ex-situ methods using acidic solutions suffer from artifacts due to adsorption of anions on the electrode surface.

The problems studied in this program were the analysis of both adsorbed and desorbed species originating from operating membrane electrode assemblies. Two systems were studied, (1) direct methanol fuel cells and (2) the isomerization reactions of olefins on fuel cell cathode electrode surfaces.

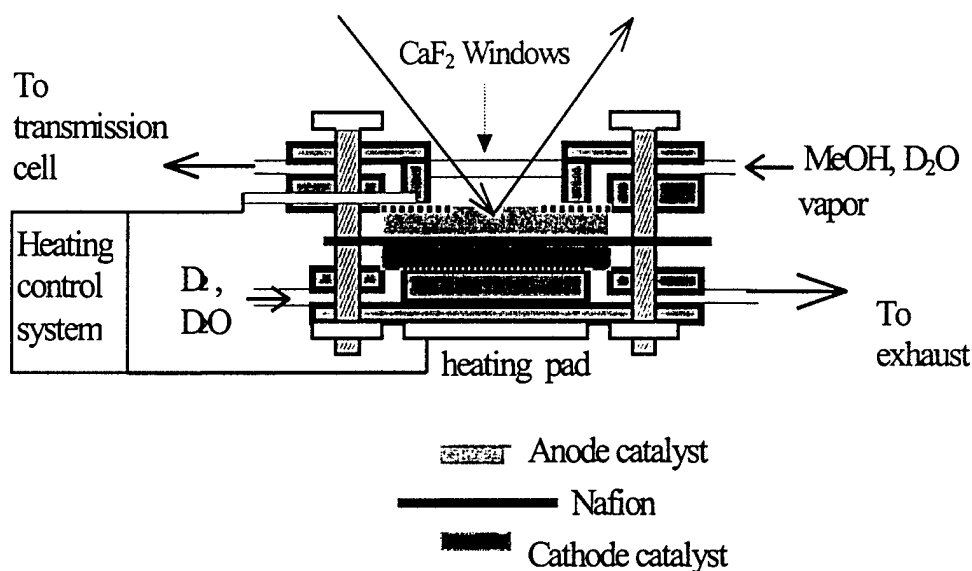
### (5) Summary of the most important results

#### 1. NEMCA

The most important result was a very new and novel development in the area of non-Faradaic electrochemical modification of catalytic activity (NEMCA), which was confirmed using the mass spectrometer and FTIR obtained in this grant. We demonstrated that the application of an applied potential to an electrode surface significantly enhances the rate of olefin isomerization reactions. These are non-electrochemical reactions. This was published in JACS with a follow-up paper in Solid State Ionics. This area of research has attracted sufficient attention to warrant an invited presentation at an upcoming NEMCA International Workshop to be held in Washington, D.C. in May of 2001. NSF and EPRI are sponsoring this meeting.

#### 2. In-Situ Electrochemical Studies of Model Surfaces and Real Membrane Electrode Assemblies by FTIR

A new surface-transmission FTIR spectroelectrochemical method was introduced by our lab. Potential dependent, *in-situ* surface reflective and on-line transmission FTIR spectroscopy of adsorbed and desorbed species, formed on direct methanol fuel cell (DMFC) anode catalytic surfaces, confirm linear bound CO as the primary intermediate on Pt black surfaces of fuel cell membrane electrode assemblies. A schematic of the cell is shown in Fig. 1.



The extent of dipole-dipole coupling and band position was found to be dependent on the methanol/water ratio. It is observed the linear Stark regime extends beyond 1.0 volt versus a deuterium reference electrode on the membrane electrode assembly catalyst surface. In addition to CO<sub>2</sub>, methylformate is a major product of a gas fed DMFC, which is detected at the anode exhaust by on line FTIR. The dual surface-transmission FTIR analysis of the fuel cell permits differentiation between adsorbed CO and an overtone of methanol that absorbs in the same frequency range as adsorbed CO. A key finding of this study is that the Stark tuning rates (shift of the IR peak position with applied potential) are much smaller on high surface area catalysts than on smooth polished electrodes.

(6)

a. Papers published in peer reviewed journals:

1. L. Ploense, Maria Salazar, Bogdan Gurau and E. S. Smotkin, "Proton Spillover Promoted Isomerization of n-Butylenes on Pd-Black Cathodes/Nafion 117," *J. Am. Chem. Soc.*, **119**, 11550-11551 (1997)
2. Renxuan Liu, Hakim Iddir, Qinbai Fan, Guoyan Hou, Aili Bo, Kevin L. Ley, E. S. Smotkin, Y. -E. Sung<sup>+</sup>, H. Kim, S. Thomas, A. Wieckowski "Potential Dependent Infrared Absorption Spectroscopy of Adsorbed CO and X-ray Photoelectron Spectroscopy of Arc-melted Single Phase Pt, PtRu, PtOs, PtRuOs and Ru Electrodes," *J. Phys. Chem. B*, **104**, 3518-3531 (2000).
3. Aili Bo, Sophia Sanicharane, Bhaskar Sompalli, Qinbai Fan, Bogdan Gurau, Renxuan Liu, and E. S. Smotkin, "In Situ Stark Effects with Inverted Bipolar Peaks for Adsorbed CO on Pt Electrodes in 50 C Direct Methanol Fuel Cells", *J. Phys. Chem. B*; **104** (31); 7377-7381 (2000)

4. Lloyd Ploense, Maria Salazar, Bogdan Gurau, E.S. Smotkin, "Spectroscopic study of NEMCA Promoted Alkene Isomerizations at PEM Fuel Cell Pd-Nafion Cathodes", **Solid State Ionics** 136-137 (0); 713-720 (2000)

**d. Manuscripts submitted but not published.**

Sophia Sanicharane, Aili Bo, Bhaskar Sompalli and E. S. Smotkin, *In-situ* 50°C Tandem Surface-reflective/Exhaust-transmission Spectroscopy of Direct Methanol Fuel Cell Membrane Electrode Assemblies, submitted to the Journal of Electrochemistry

(7) Participating Scientific Personnel

1. Lloyd Ploense:	BS	(May 1997)	Chemical Engineering
2. Maria Salazar:	PhD	(May 2000)	Chemical Engineering
3. Bogdan Gurau:	MS	(May 2000)	Chemical Engineering
4. Gouyan Hou:	PhD	Candidate	Chemical Engineering

(8) No inventions

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Abstract